

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 717 065 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

19.06.1996 Bulletin 1996/25

(51) Int Cl.⁶: **C08G 77/442**, C08G 81/02

// C08L83:04

(21) Application number: **95308376.3**

(22) Date of filing: **22.11.1995**

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: **28.11.1994 JP 317510/94**

(71) Applicant: **Dow Corning Toray Silicone Co., Ltd.**
Chuo-ku, Tokyo (JP)

(72) Inventors:

- **Furukawa, Haruhiko,**
Dow Corning Toray Silicone Co.
Ichihara-shi, Chiba Prefecture (JP)

- **Nakamura, Akihiro,**
Dow Corning Toray Silicone Co.
Ichihara-shi, Chiba Prefecture (JP)
- **Shirahata, Akihiko,**
Dow Corning Toray Silicone Co.
Ichihara-shi, Chiba Prefecture (JP)

(74) Representative: **Kyle, Diana**
Elkington and Fife
Prospect House
8 Pembroke Road
Sevenoaks, Kent TN13 1XR (GB)

(54) **Method for the preparation of thermoplastic resin composition**

(57) A method for preparing a thermoplastic resin composition, said method comprising hot-kneading, in the absence of a radical-generating catalyst,

(A) 100 parts by weight of a thermoplastic resin; and

(B) 0.1 to 200 parts by weight of an alkenyl-functional polyorganosiloxane filled with amorphous silica, wherein the weight ratio of said silica to said alkenyl-functional polyorganosiloxane is 0.01:100 to 50:100, whereby the polyorganosiloxane of component (B) is chemically bonded to resin (A).

EP 0 717 065 A1

Description

This invention relates to a highly productive method for the preparation of thermoplastic resin compositions in which a thermo-plastic resin and a polyorganosiloxane are homogeneously dispersed and chemically bonded to each other.

There have been numerous attempts at improving the moldability, surface lubricity, release properties, and water repellency of thermoplastic resins by blending therein a polyorganosiloxane, for example, dimethylpolysiloxane. Unfortunately, polyorganosiloxane bleed from the surface occurs both during and after molding operations on the thermoplastic resin compositions afforded by the prior art methods. This causes such problems as a decline in surface lubricity and a reduced mechanical strength. Polyorganosiloxane bleed also causes other problems, such as contamination of the surrounding equipment.

Chemical reaction between the thermoplastic resin and polyorganosiloxane has also been pursued to solve these problems. For example, polypropylene resin and polyorganosiloxane have been reacted in the presence of a radical-generating catalyst (graft reaction) to induce chemical bonding JP-A's 52-36898 and 6-16824. In these latter methods, however, the radical reaction between the polypropylene resin and the vinyl-functional polyorganosiloxane develops locally, which produces a poor dispersibility of the polyorganosiloxane within the polypropylene resin. This results in compositions having poor mechanical strength.

We have now found a method of production that makes possible execution of the graft reaction between the thermoplastic resin and the polyorganosiloxane under conditions which more readily support and facilitate production.

The present invention takes as its object the introduction of a method for the preparation of thermoplastic resin compositions which, after molding, are free of polyorganosiloxane bleed at the surface and which exhibit excellent properties, such as surface lubricity and mechanical strength.

The present invention therefore introduces a method for the preparation of thermoplastic resin compositions, said method comprising hot-kneading, in the absence of a radical-generating catalyst,

(A) 100 weight parts of a thermoplastic resin and

(B) 0.1 to 200 weight parts of an alkenyl-functional polyorganosiloxane filled with amorphous silica, with the proviso that the silica to alkenyl-functional polyorganosiloxane weight ratio falls in the range from 0.01:100 to 50:100,

whereby said polyorganosiloxane in component (B) becomes chemically bonded to said thermoplastic resin (A).

No specific restrictions apply to the type of the thermoplastic resin (A) used by the present invention as long as it is plasticized by heat and thereby reacts with the alkenyl-functional polyorganosiloxane in component (B). Thermoplastic resin (A) encompasses the polymers and copolymers derived from vinylic monomers, and its preferred embodiments are resins obtained by the polymerization of one or more vinylic monomers and copolymers between such resins and other resins. The thermoplastic resin is exemplified by polyethylene, polypropylene, polymethylpentene, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polyvinylidene fluoride, polystyrene, polymethyl methacrylate, polyethyl methacrylate, polybutyl methacrylate, polymethyl acrylate, polyethyl acrylate, and polybutyl acrylate; and by copolymers composed of two or more of the preceding, such as ethylenepropylene copolymers, ethylene-vinyl acetate copolymers, ethylene-vinyl chloride copolymers, ethylene-methyl methacrylate copolymers, styreneacrylonitrile copolymers, styrene-acrylonitrile-butadiene copolymers, and so forth.

The thermoplastic resin (A) of the present invention is preferably substantially free of antioxidant. This means that antioxidant has not been purposely blended into the thermoplastic resin after its polymerization. This condition, however, does not exclude trace amounts of additive, still capable of functioning as an antioxidant, that may remain from additive already present in, or added to, the starting monomer for the polymerization process, and unconsumed or unremoved after completion of the polymerization process. The content of such antioxidant preferably does not exceed 0.01 weight%, and more preferably does not exceed 0.001 weight% of component (A).

Component (B) consists of alkenyl-functional polyorganosiloxane into which amorphous silica has been blended. Its use makes possible the reaction between component (A) and the alkenyl-functional polyorganosiloxane in component (B) under conditions which more readily support and facilitate the preparation of our composition when components (A) and (B) are hot-kneaded. The amorphous silica powder of component (B) is exemplified by fumed silica, wet-process silica, and such silicas which are treated with, for example, organosilane, organosilazane, or organopolysiloxane. Preferred among these are ultrafine silicas having particle diameters no greater than 50 micrometers and specific surfaces of at least 50 m²/g.

The polyorganosiloxane bearing Si-bonded alkenyl reacts with, and chemically bonds to, the thermoplastic resin (A). This reaction is also typically known as a graft reaction. The polyorganosiloxane must contain at least 1 silicon-bonded alkenyl group in each molecule, and its molecular structure may be straight chain, partially branched, or cyclic. The alkenyl group, which is required for the development of a graft reaction between the thermoplastic resin (A) and the Si-bonded alkenyl-functional polyorganosiloxane of (B), is exemplified by vinyl, propenyl, butenyl, pentenyl, hexenyl, and so forth.

nyl, and decenyl. The non-alkenyl silicon-bonded organic groups are nonexhaustively exemplified by the hydroxyl group; substituted and unsubstituted alkyl groups, such as methyl, ethyl, propyl, 3,3,3-trifluoropropyl, and 3-chloropropyl; substituted and unsubstituted cycloalkyl groups, such as cyclopentyl and cyclohexyl; substituted and unsubstituted aryl groups, such as phenyl, or xyl; substituted and unsubstituted aralkyl groups, such as benzyl, phenethyl, or 3-phenylpropyl; and substituted or unsubstituted alkoxy groups, such as methoxy, ethoxy, and propoxy.

The polyorganosiloxane of (B) is exemplified by dimethylvinylsiloxyl-endblocked polydimethylsiloxanes, dimethylvinylsiloxyl-endblocked dimethylsiloxane-methylvinylsiloxane copolymers, trimethylsiloxyl-endblocked polymethylvinylsiloxanes, trimethylsiloxyl-endblocked dimethylsiloxane-methylvinylsiloxane copolymers, dimethylhexenylsiloxyl-endblocked polydimethylsiloxanes, dimethylhexenylsiloxyl-endblocked dimethylsiloxane-methylhexenylsiloxane copolymers, trimethylsiloxyl-endblocked polymethylhexenylsiloxanes, and trimethylsiloxyl-endblocked dimethylsiloxane-methylhexenylsiloxane copolymers.

The alkenyl-functional polyorganosiloxane preferably has a viscosity at 25°C of at least 1 million mm²/s (centistokes), while viscosities of at least 5 million mm²/s (centistokes) are even more preferred.

Moreover, the alkenyl-functional polyorganosiloxane preferably contains no more than 50,000 ppm (weight parts per million), and more preferably no more than 20,000 ppm, of low-molecular-weight siloxane having a vapor pressure equal to or greater than 1.33 kPa (10 mmHg) at 200°C.

Component (B) of the present invention consists of the mixture of the above-described amorphous silica with the above-described alkenyl-functional polyorganosiloxane. The amorphous silica micropowder to alkenyl-functional polyorganosiloxane mixing ratio must fall in the range from 0.01:100 to 50:100 on a weight basis and preferably falls in the range from 0.1:100 to 30:100 on a weight basis. Silica weight proportions below 0.01:100 are undesirable because at such values the graft reaction will not occur under conditions that support and facilitate preparation of our composition. Silica weight proportions above 50:100 are also undesirable because they yield thermoplastic resin compositions with an unsatisfactory surface lubricity, water repellency, and release performance.

The component (B) used of the present invention is prepared simply by mixing the amorphous silica with the above-described alkenyl-functional polyorganosiloxane to homogeneity using the usual mixing equipment, for example, a 2-roll mill, Ross mixer, or Henschel™ Mixer.

The components (A) and (B) are hot-kneaded in the absence of a radical-generating catalyst in our preparative method. Hot-kneading functions to interdisperse and mix components (A) and (B). Also, by radical generation in component (A) due to the heat and shear energy applied to the system, this kneading initiates and advances the graft reaction of component (A) with component (B). By adjusting the induction period until graft reaction initiation (hereinafter the induction period) and the rate of reaction development through selection of the kneading temperature and kneading rate, it is possible in our process to initiate, develop, and complete the graft reaction after having achieved a thorough dispersion of components (A) and (B). Moreover, this hot-kneading must be conducted in the absence of a radical-generating catalyst. Components (A) and (B) will react locally in the presence of such a catalyst, and a homogeneous thermoplastic resin composition will not be obtained.

The kneading time must be sufficient for the dispersion and mixing of components (A) and (B) and for the ensuing initiation, development, and completion of the graft reaction. In specific terms, the necessary kneading time is preferably from 1 to 60 minutes. The time necessary for the ensuing initiation, development, and completion of the graft reaction is also preferably from 1 to 60 minutes.

Higher kneading temperatures and higher kneading rates each lead to a shorter induction period and a more rapid rate of reaction development. With these considerations, the optimal kneading temperature and kneading rate for the instant process must be selected to satisfy both the kneading time required for dispersion and mixing of components (A) and (B), and the kneading time necessary for the subsequent initiation, development, and completion of the graft reaction. In specific terms, the preferred range for the kneading temperature is from 150°C to 260°C. The kneading rate is then determined to bring the induction period and rate of reaction development into their preferred ranges.

The equipment used in our preparative method can be those batch kneaders and heated continuous-kneaders that are generally used for kneading thermoplastic resins. The kneading efficiency, kneading rate, and so forth depend on the design of the equipment. Thus, the following are preferred for their ability to generate a sufficient level of shear energy: the Banbury™ Mixer among the batch devices, and, among the continuous devices, the continuous twin-screw kneading extruders and continuous kneading extruders equivalent in efficiency to said twin-screw extruders. Among these, the twin-screw kneading extruders are particularly preferred for their high kneading efficiencies and high heating and radiation efficiencies.

The preparative method of this invention induces the chemical bonding of component (B) to component (A), wherein the reaction and chemical bonding of at least 50 weight% of the alkenyl-functional polyorganosiloxane in component (B) is preferred, and the reaction and chemical bonding of at least 70 weight% of the polyorganosiloxane of component (B) is particularly preferred. Reaction conversions below 50 weight% result in such problems as bleed of the polyorganosiloxane of component (B) from the resulting thermoplastic resin composition and a decline in the mechanical properties thereof.

Insofar as the object of the claimed invention is not impaired, the various modifiers and additives generally used in conjunction with thermoplastic resins may also be added in our preparative method, either during or after the hot-kneading process. These are exemplified by molding improvers such as dimethylpolysiloxane, methylphenylsiloxane, polydiphenylsiloxane, and polymethyl(3,3,3-trifluoropropyl)siloxane; antistatics; pigments; and so forth.

Moreover, our preparative method permits the blending of antioxidants into the product mixture after the hot-kneading of components (A) and (B). In fact, when molding operations are preformed on the thermoplastic resin composition of our preparative method the addition of antioxidant is preferred since this can inhibit oxidative decomposition of the composition. The antioxidant should be added at from 0.1 to 5 weight parts and more preferably at from 0.1 to 2 weight parts, per 100 weight parts of the total quantity of components (A) and (B). The nature of the antioxidant is not critical, and the following are used: phenolics, amines, quinolines, hydroquinolines, mercaptans and sulfides, dithio acids, and phosphites. The phenolics are exemplified by 2,6-di-tert-butyl-4-methylphenol, 2,4-dimethyl-6-tert-butylphenol, 3-tert-butyl-4-hydroxyanisole, 2,6-di-tert-butyl-4-methylphenol, and styrenated phenols; the amines are exemplified by phenyl-alpha-naphthylamine, phenyl-beta-naphthylamine, diphenylamine, and N,N'-diphenyl-p-phenylenediamine; the mercaptans and sulfides are exemplified by dodecyl mercaptan, tetramethylthiuram disulfide, and phenothiazine; the dithioacids are exemplified by zinc ethylphenyldithiocarbamate; and the phosphites are exemplified by triphenyl phosphite, diphenyldecyl phosphite, and phenyldidecyl phosphite.

The thermoplastic resin compositions afforded by our preparative method have excellent mechanical properties, moldability, mold-releasability, surface lubricity, and so forth. As a consequence, they are useful as molding resins. They are also useful as additives for improving the physical properties of a variety of thermoplastic resins.

Examples

The present invention will be further explained in greater detail through working examples. In the examples, "parts" denotes "weight parts," the viscosity is the value measured at 25°C, and "cSt" is an abbreviation for "centistokes". The following methods were used in the examples to measure the graft reaction conversion, average dispersed particle diameter of the polyorganosiloxane phase, and surface condition of the molding.

Measurement of the graft reaction conversion

A 2 g thermoplastic resin composition sample was cut into approximately 1 mm cubes and placed in a round-bottom flask equipped with a reflux condenser. One hundred grams of hexane were added, followed by heating under reflux for 1 hour. After filtering off the hexane insolubles and transfer to a glass dish, the hexane was eliminated by heating at 60°C. Weighing then gave the hexane extraction proportion. The graft reaction conversion was calculated as indicated below from the hexane extraction proportion and the total polyorganosiloxane content in the sample.

$$\text{graft reaction conversion} = (\text{total polyorganosiloxane content in the sample} - \text{hexane extraction proportion}) \times 100 / \text{total polyorganosiloxane content in the sample}.$$

Measurement of the average particle diameter of the polyorganosiloxane phase in the thermoplastic resin composition

A sample of the thermoplastic resin composition was cooled with liquid nitrogen and then crushed. The number average particle diameter of the polyorganosiloxane phase dispersed in the thermoplastic resin composition was determined by analyzing the fracture surface with a scanning electron microscope and an x-ray microanalyzer.

Surface condition of the molding

The thermoplastic resin composition was compression molded at 180°C to give a 2 mm-thick sheet. The surface of this sheet was visually inspected for uniformity and polyorganosiloxane bleed, and the results of this inspection were reported according to the following scale.

++ : uniform surface, no polyorganosiloxane bleed
 + : uniform surface, but polyorganosiloxane bleed is observed
 x : nonuniform surface, polyorganosiloxane bleed is observed

Example 1

Two hundred grams of a dimethylvinylsiloxy-endblocked dimethylsiloxane-methylvinylsiloxane copolymer (viscosity = 10,000 mm²/s (cSt), dimethylsiloxane unit : methylvinylsiloxane unit molar ratio = 99.4 to 0.6) and 6.0 g of a fumed silica with a specific surface of 200 m²/g were mixed on a two-roll mill at room temperature to give a translucent

fluid. This fluid (10.3 g) and 15.0 g of an ethylene-vinyl acetate copolymer (Evatate™ K2010, a product of Sumitomo Chemical Company, Limited) were placed in a 30 cm³ LabPlast™ Mill and mixed for 5 minutes at 100 rpm to give a solid, white thermoplastic resin composition. The graft reaction conversion and average particle diameter of the polyorganosiloxane phase were measured on the obtained thermoplastic resin composition, and the surface condition of a molding prepared therefrom was also evaluated. These results are reported in Table 1.

Example 2

A solid, white thermoplastic resin composition was prepared as in Example 1, but in this case using a dimethylvinylsiloxy-endblocked dimethylsiloxane-methylhexenylsiloxane copolymer (viscosity = 10,000,000 mm²/s (cSt), dimethylsiloxane unit to methylhexenylsiloxane unit molar ratio = 99.4 to 0.6) in place of the dimethylvinylsiloxy-endblocked dimethylsiloxane-methylvinylsiloxane copolymer that was used in Example 1. The properties of the obtained thermoplastic resin composition were measured as in Example 1, and these results are also reported in Table 1.

Example 3

A solid, white thermoplastic resin composition was prepared as in Example 1, but in this case using a linear low-density polyethylene resin (Sumikathene-L™ FA201-0, a product of Sumitomo Chemical Company, Limited) in place of the ethylene-vinyl acetate copolymer that was used in Example 1. The properties of the obtained thermoplastic resin composition were measured as in Example 1, and these results are reported in Table 1.

Example 4

A solid, white thermoplastic resin composition was prepared as in Example 1, but in this case using an ethylene-methyl methacrylate copolymer (Acryft™ WD301, a product of Sumitomo Chemical Company, Limited) in place of the ethylene-vinyl acetate copolymer that was used in Example 1. The properties of the obtained thermoplastic resin composition were measured as in Example 1, and these results are also reported in Table 1.

Comparative Example 1

Fifteen grams of an ethylene-vinyl acetate copolymer (Evatate™ K2010, a product of Sumitomo Chemical Company, Limited) and 10.0 g of a dimethylvinylsiloxy-endblocked dimethylsiloxane-methylvinylsiloxane copolymer (viscosity = 10,000,000 mm²/s (cSt), dimethylsiloxane unit to methylvinylsiloxane unit molar ratio = 99.4 to 0.6) were placed in a 30 cm³ LabPlast™ Mill and mixed for 5 minutes at 100 rpm to give a solid, white thermoplastic resin composition. The graft reaction conversion and average particle diameter of the polyorganosiloxane phase were measured on the obtained thermoplastic resin composition, and the surface condition of a molding prepared therefrom was also evaluated. These results are listed in Table 1.

Comparative Example 2

A solid, white thermoplastic resin composition was prepared as in Comparative Example 1, but in this case replacing the 15.0 g of ethylene-vinyl acetate copolymer used in Comparative Example 1 with an ethylene-vinyl acetate copolymer mixture prepared by mixing 0.2 g of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, as a hexane solution, into 15.0 g of the ethylene-vinyl acetate copolymer used in Comparative Example 1, and thereafter drying. The graft reaction conversion and average particle diameter of the polyorganosiloxane phase were measured on the obtained thermoplastic resin composition, and the surface condition of a molding prepared therefrom was also evaluated. These results are also listed in Table 1.

Comparative Example 3

A solid, white thermoplastic resin composition was prepared as in Comparative Example 1, but in this case using a dimethylvinylsiloxy-endblocked dimethylsiloxane-methylhexenylsiloxane copolymer (viscosity = 10,000,000 mm²/s (cSt), dimethylsiloxane unit to methylhexenylsiloxane unit molar ratio = 99.4 to 0.6) in place of the dimethylvinylsiloxy-endblocked dimethylsiloxane-methylvinylsiloxane copolymer that was used in Comparative Example 1. The properties of the obtained thermoplastic resin composition were measured as in Example 1, and these results are shown in Table 1.

Comparative Example 4

A solid, white thermoplastic resin composition was prepared as in Comparative Example 1, but in this case using a linear low-density polyethylene resin (Sumikathene-L™ FA201-0, a product of Sumitomo Chemical Company, Limited) in place of the ethylene-vinyl acetate copolymer that was used in Comparative Example 1. The properties of the obtained thermoplastic resin composition were measured as in Example 1, and these results are also shown in Table 1.

Comparative Example 5

A solid, white thermoplastic resin composition was prepared as in Comparative Example 1, but in this case using an ethylene-methyl methacrylate copolymer (Acrylt™ WD301, a product of Sumitomo Chemical Company, Limited) in place of the ethylene-vinyl acetate copolymer that was used in Comparative Example 1. The properties of the obtained thermoplastic resin composition were measured as in Example 1, and these results are reported in Table 1.

Table 1

	graft reaction conversion (%)	average dispersed particle diameter of the polyorganosiloxane phase (micrometers)	surface condition of the molding	overall evaluation
Example 1	91	15	++	++
Example 2	90	10	++	++
Example 3	85	15	++	++
Example 4	93	15	++	++
Comp. Example 1	29	15	+	x
Comp. Example 2	95	100	x	x
Comp. Example 3	31	10	+	x
Comp. Example 4	21	15	+	x
Comp. Example 5	28	15	+	x

Claims

1. A method for preparing a thermoplastic resin composition, said method comprising hot-kneading, in the absence of a radical-generating catalyst, (A) 100 parts by weight of a thermoplastic resin; and (B) 0.1 to 200 parts by weight of an alkenyl-functional polyorganosiloxane filled with amorphous silica, wherein the weight ratio of said silica to said alkenyl-functional polyorganosiloxane is 0.01:100 to 50:100, whereby said polyorganosiloxane of component (B) becomes chemically bonded to said thermoplastic resin (A).
2. The method according to claim 1, wherein at least 50 weight percent of said alkenyl-functional polyorganosiloxane in component (B) is chemically bonded to said thermoplastic resin (A).
3. The method according to claim 1, wherein said thermoplastic resin (A) is a homopolymer or copolymer derived from a vinylic monomer.
4. The method according to claim 2, wherein the viscosity of said alkenyl-functional polyorganosiloxane in component (B) is at least 1 million centistokes at 25°C.
5. The method according to claim 1, wherein the diameter of said silica particles is ≤50 micron-meters and the specific surface area of said silica is at least 50 m²/g.
6. The method according to claim 1, wherein the hot-kneading is carried out at a temperature of 160°C to 260°C.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 8376

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-4 196 731 (LAURIN D.G. ET AL) 8 April 1980 * claims 19,21,23 * * column 4, line 22 - line 27 * * example 6 *	1-6	C08G77/442 C08G81/02 //C08L83:04
X	US-A-4 273 691 (MACLAURY M.R. ET AL) 16 June 1981 * claims 1,6,9,10 * * column 3, line 7 - line 14 * * example 2 *	1,3	
D,A	US-A-3 865 897 (FALENDER J.R. ET AL) 11 February 1975 * claims 1,9 * * example 1 *	1	
A	US-A-4 252 195 (BARTOS D.M.) 24 February 1981 * claim 1 * * column 5, line 6 - line 14 *	1	
A	US-A-2 888 419 (SAFFORD M.M.) 26 May 1959 * claim 1 * * column 2, line 36 - line 47 *	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 March 1996	Examiner Niaounakis, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 01.92 (P04C01)

THIS PAGE BLANK (USPTO)